

## CLEANING METHOD

This invention relates to a method of softening water and/or in which the deposition of hard water scale is inhibited. The invention relates in particular to such a method carried out in a domestic environment, in particular in ware-washing machines. The invention also relates to compressed water-softening compositions for such methods.

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It is well known that certain metal compounds, notably calcium compounds, when present in water, have a significant effect on the properties of the water. For example, "hard" water containing a significant loading of soluble calcium and magnesium compounds may require a large amount of soap or detergent in order to form a lather. Scale deposits can readily form from such water, for example on heating or pH change or evaporation. These can be encrustations, or watermarks left on evaporation of water droplets from, especially, a shiny surface.

There have been many proposals for removal of metal ions from aqueous solutions. In the industrial context proposals have included filter beds and polymeric filters for capturing heavy metal ions from an aqueous solution flowing within a passageway. Examples are given in EP992238A and GB20869564A. In the domestic context chelating compositions can be added to an aqueous washing solution and these can capture metal ions, such as calcium ions. Examples of chelating compositions are given in EP892040A.

Increasingly popular is the delivery of cleaning and water-softening compositions as compressed compositions, typically a tablet. These are convenient, providing a unit dosage which is easily handled. Difficulties arise in the production of such compressed compositions in balancing the needs that the compressed composition is suitably hard and non-friable under transportation conditions but yet is not so compacted that it cannot easily disintegrate. Suitable levels of "hardness" are between 150 N and 250 N (the test conditions being set out in the Example section). Suitable levels of "friability" are between 2% and 9% (the test conditions being set out in the Example section). Suitable "disintegration" times are between 5 seconds and 180 seconds, when placed in 1 l of gently stirred water at 25°C.

It is well known in the art to include a disintegrant, which will promote disintegration of the tablet in laundry detergent tablets and laundry detergent additive tablets. Various classes of disintegrants are known, including the class in which disintegration is caused by the swelling of the disintegrant. Various swelling disintegrants have been proposed in the literature, for instance in WO 98/54283, with the preference being directed predominantly towards starches, celluloses and water soluble organic polymers. Furthermore, inorganic swelling disintegrants such as bentonite clay have also been mentioned, for instance in EP-A-0 466 484.

We have found that water-softening compositions are particularly difficult compositions to compress and retain as a compressed solid. This is mainly due to the high content of crystalline solids (as compared to  
5 detergent tablets that contain higher amounts of organic molecules, such as surfactant), for example, citrate salts and silicates, that do not easily bind together. Therefore, much higher compression forces are needed to produce suitable compressed compositions. Compression  
10 forces used are greater than 35KN, 40KN, 45KN or 50KN. However, compression forces are usually less than 100KN, 95KN, 90KN, or 85KN.

We have found a particularly suitable water softening  
15 composition for the formation of a compressed composition that provides high levels of hardness of at least 100N, 150N, 175N or 200N. Hardness levels are usually less than 300N, 275N or 250N. An acceptably low level of friability of less than 15%, 10% or 8%. Low disintegration times of  
20 less than 1 minute are achieved ideally between 20 and 30 seconds.

EP 0812808 discloses water-softening tablets containing disintegrants.

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Therefore, we present as a first feature of the invention a compressed water softening composition comprising at least one water-softening active and a blend of disintegrating agents comprising

- 30 (a) cross linked polyplasdone;  
(b) a water-swellaable cellulose; and, optionally,  
(c) a water-soluble salt.

By the use of the term water-softening composition we mean that the composition is substantially free of surfactant and/or bleach ingredients, i.e. less than 5% or 1% by weight, ideally 0% by weight.

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As discussed above, water softening compositions are characterised in that they contain large amounts of water softening active ingredients that are crystalline material, i.e. more than 35% by weight, more than 38% by weight, more than 40% by weight or more than 42% by weight.

Typical crystalline materials include citrate salts, zeolites, silicates and clays. Preferably such crystalline materials are selected from citrate salts or silicate.

The blend of disintegrating agents is present in an amount of up to 10%, 8%, 7%, 6%, 5%, 3% or 2% wt of the composition. The blend of disintegrating agents is present in an amount of at least 0.1%, 0.3%, 0.5%, 0.7%, 0.9%, 1.1%, 1.3%, 1.5% or 1.7% wt of the composition.

#### 25 Water Softening Active

Water-softening actives are present in the composition in an amount of at least 40%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85% or 90% by weight of the composition. Maximum amounts of water-softening actives are present in an amount of less than 99%, 97%, 93%, 90%, 87%, 83% or 80% by weight of the composition.

There are three main types of method of action for water softening actives, described below.

- 5        1) Ion exchange agents - such agents include alkali metal (preferably sodium) aluminosilicates either crystalline, amorphous or a mixture of the two. Such aluminosilicates generally have a calcium ion exchange capacity of at least 50 mg CaO per gram of  
10 aluminosilicate, comply with a general formula:



and incorporate some water. Preferred sodium  
15 aluminosilicates within the above formula contain 1.5-3.0 SiO<sub>2</sub> units. Both amorphous and crystalline aluminosilicates can be prepared by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

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Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1429143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well known  
25 commercially available zeolites A and X, and mixtures thereof. Also of interest is zeolite P described in EP 384070 (Unilever).

Another class of compounds are the layered sodium  
30 silicate builders, such as are disclosed in US-A-4464839 and US-A-4820439 and also referred to in EP-A-551375.

These materials are defined in US-A-4820439 as being crystalline layered, sodium silicate of the general formula



where

M denotes sodium or hydrogen,  
10 x is from 1.9 to 4 and y is from 0 to 20.

Quoted literature references describing the preparation of such materials include Glastechn. Ber. 37,194-200 (1964), Zeitschrift für Kristallogr. 129, 396-  
15 404 (1969), Bull. Soc. Franc. Min. Crist., 95, 371-382 (1972) and Amer. Mineral, 62, 763-771 (1977). These materials also function to remove calcium and magnesium ions from water, also covered are salts of zinc which have also been shown to be effective water softening  
20 agents.

2) Ion capture agents - agents which prevent metal ions from forming insoluble salts or reacting with surfactants, such as polyphosphate, monomeric  
25 polycarbonates, such as citric acid or salts thereof, EDTA, algins, alginates.

3) Anti-nucleating agents - agents which prevent seed crystal growth, such as polycarbonate polymers, such as  
30 polyacrylates, acrylic/maleic copolymers, and acrylic phosphonates, and sulfonates.

Water-soluble salt

The water-soluble salt is an optional, but preferred, constituent of the disintegrant blend. Ideally it is present in amounts of up to 0.1% possibly up to 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 or 1.4% by weight of the composition. Ideally the water-soluble salt is provided as at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80% or 85% by weight of the disintegrant blend. Ideally the water-soluble salt is provided as no more than 95%, 90%, 85%, 80%, 75%, 70%, 65%, 60%, 55%, 50%, 45%, 40%, 35%, 30%, 25%, 20%, 15% or 10% by weight of the disintegrant blend.

Ideally the water-soluble salt has a solubility of at least 50 g/100 g in deionized water at 20°C. This is an exceptionally high solubility: many materials which are classified as water-soluble are less soluble. Suitable highly water-soluble materials which may be used are selected from, with their solubilities expressed as grams of solid to form a saturated solution in 100 g of deionized water at 20°C: potassium acetate >200, potassium carbonate 112, urea > 100, sodium acetate anhydrous 119, sodium acetate trihydrate 76 and magnesium sulphate. 7H<sub>2</sub>O 71 or mixtures thereof.

The rapid dissolution of the water-soluble salt provides rapid ingress of water into the tablet, thus not only affecting the tablet's integrity, but allowing water to rapidly access the other disintegrant components within the tablet, particularly the swelling disintegrants.



By contrast the solubilities of some other common materials at 20°C are: sodium chloride 36, sodium sulphate decahydrate 21.5, sodium carbonate anhydrous 6.0, sodium percarbonate anhydrous 12, sodium perborate 5 anhydrous. Preferably this highly water soluble material is incorporated as particles of the material in a substantially pure form (i.e. each such particle contains over 95% by weight of the material).

#### 10 Cross Linked Polyplasdone

Ideally present in the composition in amounts of up to 0.1% possibly up to 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 or 1.4% by weight of the composition. Ideally the cross 15 linked polyplasdone is provided as at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80% or 85% by weight of the disintegrant blend. Ideally the cross linked polyplasdone is provided as no more than 95%, 90%, 85%, 80%, 75%, 70%, 65%, 60%, 55%, 20 50%, 45%, 40%, 35%, 30%, 25%, 20%, 15% or 10% by weight of the disintegrant blend.

Cross linked polyplasdone consists of N-vinyl-2-pyrrolidone polymerised and cross-linked simultaneously by a reaction known as "pop-corn" polymerisation. The 25 unique structure of cross linked polyplasdone (sometimes referred to as crosopovidone) provides superior adsorptive capacity and exceptional swelling rate. Suitable methods for preparing cross linked polyplasdone can be found in EP 1263814 & EP 1036839.



Water-swellable Cellulose

Ideally present in the composition in amounts of up  
5 to 0.1% possibly up to 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 or  
1.4% by weight of the composition. Ideally the water-  
swellable cellulose is provided as at least 5%, 10%, 15%,  
20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%,  
75%, 80% or 85% by weight of the disintegrant blend.  
10 Ideally the water-swellable cellulose is provided as no  
more than 95%, 90%, 85%, 80%, 75%, 70%, 65%, 60%, 55%,  
50%, 45%, 40%, 35%, 30%, 25%, 20%, 15% or 10% by weight  
of the disintegrant blend.

Suitable water-swellable cellulose materials have  
15 sufficient water-absorptivity that they can absorb at  
least 15, 12, 10, 8, 6, 4, 2, 1 times their own weight of  
water, ie. a water uptake of at least 15, 12, 10, 8, 6,  
4, 2, 1 g per g of deionised water at 20°C.

A number of such materials are known, and which may  
20 be chemically modified to enhance its water uptake  
capacity. Sometimes such modified celluloses have ionic  
substituents but for this invention it is preferred that  
any substituents are nonionic.

For the avoidance of doubt water-swellable cellulose  
25 does not include microcrystalline cellulose commonly used  
in compacted compositions. Microcrystalline cellulose is  
used as a wicking agent to bring water into the compacted  
composition to aid disintegration and is not water-  
swellable, or at least is not water-swellable to the  
30 extent required in the present invention.

Microcrystalline cellulose may be included as an additional disintegrant.

The compositions may be used in ware washing using a machine or a manual method. The compositions may also be used to soften water in other cleaning methods such as hard surfaces, for example using a hand-cloth or mop, and an open vessel, for example a bucket or bowl. Thus, the cleaning method could be a method of cleaning a hard surface, for example a window, a tiled surface, shower screen, dirty tableware and kitchenware, a sanitary article, for example a bath, shower screen, lavatory, wash basin or sink, a car or a kitchen worktop.

The invention will now be described, by way of embodiment, with reference to the following Examples.

#### Examples

##### 20      Hardness Test

Using a dynamometer with a test piston diameter of 8 mm and a piston speed 30 mm per minute (a machine such as the ERWEKA tablet hardness tester THB 30 may be used) the maximum hardness of the tablet just prior to breakage is recorded for 4 tablets in the same orientation and averaged.

##### Friability Test

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Ten tablets are weighed and placed into a square plastic sample holder of approximate dimensions

110×110mm square by 170mm long. The sample holder is rotated horizontally along its length at 50 rpm for 1 minute. The tablets are weighed again and the amount of material loss expressed as percentage

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$$\% \text{ friability index} = \frac{W_0 - W_1}{W_0} \times 100$$

where:

$W_0$  = initial weight

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$W_1$  = weight of the tablets after one minute of test at 50 rpm.

The tablets were pressed at between 50 and 80N. The hardness was measured at between 180 and 260N, the friability was AROUND 4% and dissolution times of between 20 and 30 seconds were found.

Raw Materials %wt	1st region	2nd region	Total
Water softening Homopolymer	26.000	35.000	27.800
Citrate	60.500	46.000	57.600
PEG	4.500	4.000	4.400
Polyplasdone+Cellulose	9.000	9.500	9.100
Dye		0.016	0.003
Filler		5.484	1.097
TOTAL	100	100	100